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(54) **Water repellent composition, fluorocarbon polymer coating composition and coating film
therefrom**

(57) Fluorocarbon polymer coating composition and coating film include a fluorocarbon polymer powder, a binder and an additive comprised by a substance having

a surface free energy smaller than that of the binder. The coating composition and coating film have improved resistance to deterioration with time of the water repellent properties of the film.

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Description

The present invention relates to a composition containing fluorocarbon polymer powder, to a coating composition containing fluorocarbon polymer powder and a binder dispersing the powder, and to a coating film made therefrom. Films made from the fluorocarbon polymer composition or coating composition of the present invention have water repellent properties, water proofing properties, anti snow adhesion, lubricating properties so that the composition of the present invention can be used as coated on various articles which need to have water repellent properties. Articles that require water repellent properties include, for example, rain goods such as umbrellas, exteriors of buildings, outdoor constructions, automobiles, and the like. Articles or products which must have antisnow-sticking properties and antiice-sticking properties are, for example, roofs of houses or buildings located in heavy snow falling regions, antennae for radio communication, cables, steel towers, railway vehicles, ships, automobiles, jigs for civil engineering machines, and the like. Also, the fluorocarbon polymer composition and coating composition of the present invention can be used in a wide variety of applications including protective films for protecting metal articles.

Conventional fluorocarbon polymer coating compositions and films are used in various fields including construction or architecture, automobiles, and the like. These coating compositions and coating films comprise single component system consisting of a copolymer of a fluoroolefin with one or more of various other hydrocarbons. There have been used two-component coating compositions and coating films which contain polytetrafluoroethylene or polyvinylidene fluoride as a main component mixed with a specific acrylic resin. However, these conventional coating compositions and coating films do not have sufficiently high water repellent properties and the resulting films have a water contact angle of about 80°. In previous efforts, the present inventors have investigated water repellent properties of fluorocarbon polymer-based coating compositions and coating films therefrom and realized two-component coating compositions which contain a fluorocarbon polymer powder dispersed in a binder and have high water repellent properties as expressed in terms of water contact angle of about 140°. The coating compositions and coating films have been put into practical use.

However, the two-component coating compositions and coating films made therefrom associated with a problem that instead of their excellent initial water repellent properties, the coating compositions and coating films made therefrom suffer deterioration of water repellent properties when immersed in water for a prolonged period of time.

Accordingly, an object of the present invention is to obviate the above problems associated with the conventional coating compositions and coating films and provide a fluorocarbon polymer coating composition.

Another object of the present invention is to provide a fluorocarbon polymer coating film.

Still another object of the present invention is to provide a fluorocarbon polymer composition or material.

According to a first aspect, the present invention provides a fluorocarbon polymer coating composition characterized by comprising:

a fluorocarbon polymer powder;
a binder; and

an additive comprising a substance having a surface free energy smaller than that of the binder.

Here, the additive may be one substance selected from a fluoro oil, a surfactant, and mixtures thereof.

The fluoro oil may be at least one of perfluorinated polyether, perfluorinated alkyl polyether, and polytrifluoroethylene.

The surfactant may be a fluorocarbon surfactant.

The fluorocarbon polymer powder may be at least one of polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder, and mixtures thereof.

The fluorocarbon polymer powder may comprise fluorocarbon polymer having partially or completely fluorinated terminal groups.

The binder may be at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, ethylene/carbon monoxide copolymer, ethylene/vinylketone copolymer, propylene/vinylketone copolymer, styrene/vinylketone and copolymer.

The binder may be at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone and polyester resin.

The additive may preferably have a surface free energy larger than that of the perfluorinated polymer powder.

The fluorocarbon polymer powder may preferably comprise fluorocarbon polymer having an average molecular weight of 500 to 20,000.

According to a second aspect, the present invention provides a fluorocarbon polymer coating film comprising:

a fluorocarbon polymer powder;
a binder; and

an additive comprising a substance having a surface free energy smaller than that of the binder.

Here, the additive may be one substance selected from a fluoro oil, a surfactant, and mixtures thereof.

5 The fluoro oil may be at least one of perfluorinated polyether, perfluorinated alkyl polyether, and polytrifluoroethylene.

The surfactant may be a fluorocarbon surfactant.

The fluorocarbon polymer powder may be at least one of polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder, and mixtures thereof.

10 The fluorocarbon polymer powder may comprise fluorocarbon polymer having partially or completely fluorinated terminal groups.

The binder may be at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, ethylene/carbon monoxide copolymer, ethylene/vinylketone copolymer, propylene/vinylketone copolymer, styrene/vinylketone and copolymer.

15 The binder may be at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone and polyester resin.

The additive may have a surface free energy larger than that of the perfluorinated polymer powder.

The fluorocarbon polymer powder may comprise fluorocarbon polymer having an average molecular weight of 500 to 20,000.

20 The fluorocarbon polymer powder may exist in agglomerate units comprised by a mixture of the fluorocarbon polymer powder with the binder or the additive, the agglomerate unit constituting the coating film.

Gaps between particles of the fluorocarbon polymer powder may be filled with at least one of the binder and the additive.

According to a third aspect, the present invention provides a water repellent composition comprising:

25 a fluorocarbon polymer powder comprising a fluorocarbon polymer having a molecular weight of 500 to 20,000; a matrix resin selected from the group consisting of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, epoxy resin, ethylene/carbon monoxide, ethylene/vinylketone copolymer, propylene/vinylketone copolymer, styrene/vinylketone copolymer, and mixtures thereof; and

30 an additive comprising a substance having a surface free energy smaller than that of the matrix resin.

Here, the fluorocarbon polymer powder may be at least one selected from the group consisting of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, epoxy resin, and mixtures thereof.

The additive may be at least one substance selected from a fluoro oil, surfactant and mixtures thereof.

35 The fluoro oil may be at least one of perfluorinated polyether, perfluorinated alkyl polyether, and polytrifluoroethylene.

The surfactant may be a fluorocarbon surfactant.

The fluorocarbon polymer powder may be at least one of polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder, and mixtures thereof.

40 The fluorocarbon polymer powder may comprise fluorocarbon polymer having partially or completely fluorinated terminal groups.

The additive may have a surface free energy larger than that of the perfluorinated polymer powder.

According to the present invention, the composition or film contains in addition to the fluorocarbon polymer powder and the binder, an additive which is a substance having a surface free energy smaller than that of the binder. This additive fills space between the fluorocarbon polymer particles and the binder resin to prevent penetration of water into the coating film. This results in high water repellent properties which last for a prolonged period of time. In other words, with the composition and film of the present invention, a decrease in water repellency will not occur for long time even when used outdoors or with occasional or frequent exposure to water. The coating composition and coating film of the present invention have decreased snow shearing force and, hence, are excellent in antisnow-sticking properties.

50 The above and other objects, effects, features and advantages of the present invention will become more apparent from the following description of embodiments thereof taken in conjunction with the accompanying drawings.

Fig. 1A is a schematic cross-sectional view showing a water drop on a coating film according to an embodiment of the present invention;

55 Fig. 1B is a schematic diagram illustrating a water contact angle of the water drop on the coating film shown in Fig. 1A;

Fig. 2 is a graph illustrating relationship between a surface free energy of an additive and a water contact angle;

Fig. 3 is a graph illustrating time-dependent changes of water repellent properties of fluoro oil-containing coating

film samples when immersed in water;
 Fig. 4 is a graph illustrating time-dependent changes of water repellent properties of surfactant-containing coating film samples when immersed in water;
 Fig. 5A is a graph illustrating time-dependent changes of water repellent properties of coating film samples containing various amounts of fluoro oil when immersed in water;
 Fig. 5B is a graph illustrating time-dependent changes of water repellent properties of coating film samples containing various amounts of fluoro oil when immersed in water;
 Fig. 5C is a graph illustrating time-dependent changes of water repellent properties of coating film samples containing various amounts of fluoro oil when immersed in water;
 Fig. 5D is a graph illustrating time-dependent changes of water repellent properties of coating film samples containing various amounts of fluoro oil when immersed in water;
 Fig. 5E is a graph illustrating time-dependent changes of water repellent properties of coating film samples containing various amounts of fluoro oil when immersed in water;
 Fig. 6 is a graph illustrating an influence of fluoro oil content on residual water repellent properties after 200 day immersion in water;
 Fig. 7A is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil (magnification: X300);
 Fig. 7B is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil (magnification: X300);
 Fig. 7C is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil (magnification: X300);
 Fig. 7D is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil (magnification: X300);
 Fig. 8A is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film with a varied amount of fluoro oil (magnification: X1,000);
 Fig. 8B is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film with a varied amount of fluoro oil (magnification: X1,000);
 Fig. 8C is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film with a varied amount of fluoro oil (magnification: X1,000);
 Fig. 8D is a schematic diagram illustrating a surface of a fluorocarbon polymer-containing coating film with a varied amount of fluoro oil (magnification: X1,000);
 Fig. 9A is a graph illustrating a profile of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil;
 Fig. 9B is a graph illustrating a profile of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil;
 Fig. 9C is a graph illustrating a profile of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil;
 Fig. 9D is a graph illustrating a profile of a fluorocarbon polymer-containing coating film containing a varied amount of fluoro oil;
 Fig. 10A is a graph illustrating an influence of a manufacturing method for manufacturing fluorocarbon polymer powder in an oxygen-controlled environment on water repellent properties of a coating film containing the powder; and
 Fig. 10B is a graph illustrating an influence of a manufacturing method for manufacturing fluorocarbon polymer powder in an environment without oxygen control on water repellent properties of a coating film containing the polymer powder.

The conventional two-component fluorocarbon polymer coating composition forms films which have surfaces in which the fluorocarbon polymer particles and the binder do not wet with each other due to a large difference in surface free energy between the two components. The films have a structure in which part or whole of the respective fluorocarbon polymer particles emerge from the surface of the binder. With the films having such a structure, a decrease in water repellent properties due to a prolonged immersion in water is observed. This is caused by the presence of gaps formed between the fluorocarbon polymer particles and the binder. It is considered that water penetrates into the gaps gradually and trapped therein, thus causing a decrease in water repellent properties of the film. Denaturation or change in structure of the binder exposed on the surface of the film is considered to be a possible cause of a decrease in water repellent properties.

As a result of intensive investigation, the present inventors have found that the deterioration with time of water repellent properties observed with the conventional two-component fluorocarbon polymer coating compositions and films is caused by existence of gaps formed between the fluorocarbon polymer particles and the binder due to poor

wettability of the two components with each other since they have surface free energies differing considerably from each other and that removal or reduction of the gaps realizes improved water repellent properties. The present invention is completed based on this discovery.

As described above, the present invention is directed to water repellent composition, coating composition and coating film which contains fluorocarbon polymer powder and a binder and an additive which is a substance having a surface free energy smaller than that of the binder. Existence of the additive improves wettability of the fluorocarbon polymer particles with the binder so that the occurrence of gaps between the fluorocarbon polymer particles and the binder can be prevented effectively.

That is, the fluorocarbon polymer particles mix well with the additive or binder to reduce the gaps or spaces between the respective fluorocarbon polymer particles. Since the additive has a surface free energy smaller than that of the binder, the additive covers therewith the binder on the surface of the resulting coating film. In a preferred embodiment, the fluorocarbon polymer powder has a surface free energy, as fluorocarbon polymer powder which is smaller than those of the additive and binder, respectively, so that the particles of fluorocarbon polymer powder near the surface of the additive or binder emerge partly from the surface of the film and exposed to the environmental atmosphere.

From the foregoing, the structure of the coating film of the present invention is considered to comprise a mixture of the additive or binder with the fluorocarbon polymer particles with gaps between the respective fluorocarbon polymer powder being minimized or completely filled with the additive or binder. In the present invention, the binder on the surface of the coating film is covered with the additive and is not or rarely exposed to the ambient atmosphere. This is contrary to the case where a conventional two-component coating composition is used where the binder is uncovered on the surface of the resulting coating film.

For this reason, the coating film of the present invention is prevented from the occurrence of deterioration with time of water repellent properties so that a decrease in water repellent properties can be prevented even after a prolonged immersion in water.

In addition, existence of the additive that has a surface free energy smaller than that of the binder on the surface of the coating film as exposed to the ambient atmosphere decreases ice adhesion or sticking on the surface of the coating film.

The fluorocarbon polymer particles which can be used in the coating composition and coating film of the present invention includes, for example, polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder. These fluorocarbon polymer particles can be used singly or in combination.

The fluorocarbon polymer particles comprise polymers which have terminal groups that are partially fluorinated or completely fluorinated (perfluorinated).

Preferably, the fluorocarbon polymer powder has a particle size of 1 to 100 µm.

In the water repellent material, coating composition and coating film of the present invention, the fluorocarbon polymer, for example, polytetrafluoroethylene, has a molecular weight of preferably 500 to 20,000. This is because when the molecular weight of the fluorocarbon polymer is below 500, the bondings connected to carbon atoms cannot be fluorinated completely and nonfluorinated carbons tend to form carbonyl groups or the like in the skeleton that are capable of forming hydrogen bonds with molecules of water, thus deteriorating water repellent properties and waterproofing properties of the coating film.

The fluorocarbon polymer powder can be prepared by a conventional method. In this case, it is preferred that the fluorocarbon polymer powder be prepared under controlled such that high degree of fluorination can be attained and the concentration of oxygen in the ambient atmosphere is maintained at a level not higher than 0.1%.

As the binder, there can be used polyvinylidene fluorides, polytetrafluoroethylenes, acrylic silicone resins, polyesters, ethylene/carbon monoxide copolymers, ethylene/vinylketone copolymers, propylene/vinylketone copolymers, and styrene/vinylketone copolymers. These binder resins can be used singly or in combination.

The ethylene/carbon monoxide copolymers, ethylene/vinylketone copolymers, propylene/vinylketone copolymers, styrene/vinylketone copolymers and the like are photodegrading resins which photochemically decompose upon exposure to sunlight to have decreased molecular weights and tend to become brittle so that they will readily be broken down when exposed to the weather. However, these binder resins can also be used in the present invention. When the fluorocarbon polymer powder is dispersed in the above-described binder in amounts of preferably 5 to 90% by volume, a self-regenerating type water repellent coating composition can be obtained in which always new water repellent surfaces appear due to the above-described breaking down of the photodegrading resin. The preferred content of the fluorocarbon polymer powder of 5 to 90% by volume is selected for the following reasons. With below 5% by volume of the fluorocarbon polymer powder, no sufficient water repellent effect can be obtained while with above 90% by volume of the fluorocarbon polymer powder, the sunlight is shielded by the fluorocarbon polymer particles so that breaking down of the above-described binder resins is sometimes deterred, resulting in a delayed self-regeneration of water repelling effect.

The additive which can be used in the present invention is not limited particularly as far as it has a surface free energy smaller than that of the binder. Suitable binders include fluoro oils and surfactants. These can be used singly

or in combination.

Examples of the fluoro oils include perfluorinated polyethers, perfluorinated alkyl polyethers, polytrifluoroethylene, and mixtures thereof.

Preferred surfactant is, for example, a fluorocarbon surfactant.

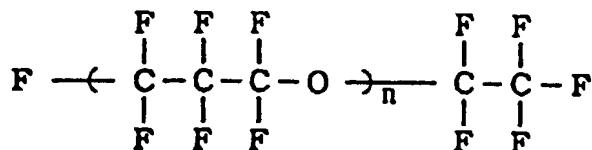
In the present invention, the surface free energy of the additive must be larger than that of the fluorocarbon polymer powder.

Among the fluoro oil and fluorocarbon surfactants, particularly preferred are those listed in Table 1 below.

Table 1

Kind of Additive	Name of Additive	Surface Free Energy (mN/m)
Fluoro Oil	Perfluorinated polyether (M.W.=2,700)	17.7
Fluoro Oil	Perfluorinated polyether (M.W.=4,500)	18.4
Fluoro Oil	Perfluorinated polyether (M.W.=5,600)	18.5
Fluoro Oil	Perfluorinated polyether (M.W.=8,400)	19.1
Surfactant	Perfluorinated alkyl carboxylic acid salt	44.6
Surfactant	Perfluorinated alkyl quaternary ammonium salt	34.0
Surfactant	Perfluorinated alkyl ethylene oxide adduct	17.4
Surfactant	Perfluorinated alkyl oligomer	26.4

*) Chemical structure of fluoro oil (perfluorinated polyether):



The coating composition of the present invention can be coated on a substrate or an article to be coated directly. Alternatively, there may be applied to the substrate or article to be coated at least one of or mixtures of resins selected from acrylic silicone resin, polyester resin, epoxy resin, acrylic resin, urethane resin, phthalic acid resin, fluorocarbon resin, vinyl resin before the coating composition of the present invention can be coated thereon. Furthermore, the water repellent coating composition of the present invention may be applied to a substrate or article after it is coated with a water repellent coating composition comprising at least one of acrylic silicone resin, polyester resin, epoxy resin, acrylic resin, urethane resin, phthalic acid resin, fluorocarbon resin, or vinyl resin and fluorocarbon polymer powder having a molecular weight of 500 to 20,000 and containing fluorinated terminal groups in amounts of 5 to 90% by volume and the volatile components therein is evaporated.

Hereafter, the present invention is described in more detail by embodiments. However, the present invention should not be construed as being limited thereto.

EMBODIMENT 1

Using a ball mill were prepared three-component formulations which consisted of 80% by volume of powder of polytetrafluoroethylene having an average molecular weight of 8,500 and a particle diameter of 4 µm as fluorocarbon polymer powder, 19.5% by volume of polyvinylidene fluoride as a binder, and 0.5% by volume of perfluorinated polyether having a varied molecular weight as a fluoro oil. As the perfluorinated polyether were used four kinds of polymers having different molecular weights: M.W.=2,700, 4,500, 5,600, and 8,400, respectively. These fluorocarbon polymer coating compositions were sprayed on respective fiber reinforced plastics (FRP) plates mainly comprised by an epoxy resin to prepare samples for evaluating the effect of the present invention. Separately, four coating composition formulations were prepared in the same way as above except that four kinds of fluorocarbon surfactants having surface free energies of 17.4, 26.4, 34.0, and 44.6 mN/m, respectively, in an amount of 0.5% by volume were used instead of the above-described fluoro oil. The resulting coating compositions were sprayed onto FRP plates mainly comprised by an epoxy resin containing glass fiber to prepare samples for evaluating the effect of the present invention.

COMPARATIVE EMBODIMENT 1

A coating composition of Comparative Embodiment 1 was prepared by mixing 80% by volume of the same polytetrafluoroethylene powder as used in Embodiment 1 and 20% by volume of polyvinylidene fluoride as a binder using a ball mill. The coating composition thus obtained was sprayed onto an FRP plate comprised mainly by an epoxy resin to prepare a comparative sample.

TEST EXAMPLE 1

First, water repellent properties of the samples obtained in Embodiment 1 and Comparative Embodiment 1 are described below.

Contact angle of water (hereafter, referred to as water contact angle) is well known as an index of water repellent properties, with larger contact angle indicating higher water repellent properties. The water repellent properties of the samples were measured using a contact angle measuring system manufactured by KYOWA KAIMEN KAGAKU CO., LTD. More particularly, a water droplet of about 4 μl ($4 \times 10^{-9}\text{m}^3$) was dropped on a surface of each coating film and water contact angles were measured. Fig. 1 is a schematic diagram illustrating a water droplet on the coating film of Embodiment 1. In Fig. 1A, a water droplet 2 is on a coating film 1. Fig. 1B is a schematic diagram illustrating measurement of water contact angle. Measurements were made at room temperature (23°C) and an average value was calculated from 5 measured values. In the case of perfluorinated polyether having a molecular weight of 2,700, water contact angle was 150° . The perfluorinated polyether having molecular weight of 4,500, 5,600, and 8,400, respectively, showed a water contact angle of 140° . Fig. 2 shows water contact angles measured when various additives having different surface free energy were added to the coating compositions. More particularly, Fig. 2 illustrates relationship between the surface free energy, (mN/m) of additive and the water contact angle ($^\circ$). In Fig. 2, filled circles indicate a surfactant-based additive, and blank squares indicate a fluoro oil-base additive. As described earlier, Table 1 lists up specific examples of fluoro oil and of surfactants used as the additive. Use of additives having surface free energies smaller than that of the binder resin gives water contact angles of not smaller than 140° . On the other hand, addition of the additive having a surface free energy larger than that of the binder results in failure of giving high water contact angles. For ease of understanding, Fig. 2 also illustrates respective average surface free energies of fluorocarbon polymer powder and polyvinylidene fluoride as a binder by dot lines (cf. Yoshiaki Kitasaki, Hata, Toshio, Nippon Sekchaku Kyokai Shi, Vol. 8, page 131 (1972), E.G. Shafrin and W.A. Zisman, Journal of Physical Chemistry, Vol. 64, page 519 (1972)).

On the other hand, the sample of Comparative Embodiment 1 had a water contact angle of 140° . From these data, it follows that addition of an additive having a surface free energy smaller than that of the binder gives a coating film having water repellent properties equivalent to those of the two-component fluorocarbon polymer coating composition.

TEST EXAMPLE 2

Next, explanation will be made of deterioration with time of water repellent properties as a result of water immersion test. Fig. 3 is a graph which illustrates relationship between period (numbers of day) of immersion in water and water repellent properties of films made from fluorocarbon polymer coating compositions containing as the additive described above four types of perfluorinated polyethers with different molecular weights, respectively, according to Embodiment 1 of the present invention. For comparison, Fig. 3 also shows water repellent properties of the sample of Comparative Embodiment 1. More particularly, Fig. 3 is a graph illustrating time dependent change in water repellent properties of fluoro oil-containing sample films when immersed in water, with the horizontal axis (axis of abscissa) indicating period of immersion in water (day) and the vertical axis (axis of ordinate) indicating water contact angle ($^\circ$). Symbols filled circle, blank circle, filled square and blank square designate the cases where the perfluorinated polyethers used had molecular weights of 2,700, 4,500, 5,600, and 8,400, respectively. Filled triangle designates the case where no additive was used. The coating film samples prepared from the coating compositions according to Embodiment 1 of the present invention were immersed in deionized water and taken out after respective predetermined days, followed by measuring water contact angles by the above-described method. This operation was repeated and evaluation was made of effects of a long-term immersion in water. The samples obtained by coating the fluorocarbon polymer coating composition of the present invention showed less deterioration with time of water repellent properties as compared with the sample of Comparative Embodiment 1 and are superior in a long-term water resistance. In particular, the sample containing the fluoro oil having a molecular weight of 2,700 retained a high initial water repellent property even after immersion in water for 100 days. As for the perfluorinated polyether used as the additive in the present invention, more preferred are those which have a molecular weight of not larger than 5,600 in view of resistance to long-term water immersion. Further, it is preferred that the fluorocarbon polymer powder is contained in an amount of not smaller than 30% by volume based on the total volume of the coating composition or film. Further, it is more preferred that the coating

composition or coating film of the present invention contain the fluorocarbon polymer powder in amounts of not less than 30% by volume. The amount of the additive is preferably not more than 10% by volume since the fluorocarbon polymer powder can be dispersed uniformly in the binder when the additive exists in amounts not more than 10% by volume.

5 The sample of Comparative Embodiment 1 was evaluated for the surface of the coating composition in the same manner as described above. As a result water contact angle of 140° was observed. Although no remarkable difference in initial water repellent properties just after formation of coating films was observed among the samples containing the fluorocarbon polymer powder having molecular weights other than 2,700, the fluorocarbon polymer coating composition and coating film of the present invention were confirmed to be superior to the conventional fluorocarbon polymer coating composition and film in resistance to long-term water immersion.

10 Fig. 4 is a graph illustrating relationship between period of immersion in water and water repellent properties of coating film samples made from the fluorocarbon polymer coating composition according to Embodiment 1 of the present invention containing 0.5% by volume of a fluorocarbon surfactant as the additive. More particularly, Fig. 4 is a graph illustrating time dependent change in water repellent properties of fluorocarbon surfactant-containing sample films when immersed in water, with the horizontal axis (axis of abscissa) indicating period of immersion in water (day) and the vertical axis (axis of ordinate) indicating water contact angle (°). As for symbols, blank square and filled triangle designate the cases where the perfluorinated polyethers used had surface free energies of 17.4 mN/m and 26.4 mN/m, respectively.

15 Evaluation of water repellent properties of the resulting film samples were made in the same manner as described above and as a result the both samples showed less decreased water repellent properties than the sample of Comparative Embodiment 1 as illustrated in Fig. 3. This clearly indicates that the samples of the invention had long-term resistance to water.

TEST EXAMPLE 3

20 In order to compare ice adhesion, ice was allowed to adhere on coating films and snow sticking shearing force was measured using a snow sticking force tester. The tester is a device with which cylindrical ice piece of 32 mm in diameter deposited on the surface of a coating film sample is pulled at a constant speed in the direction parallel to the surface of the coating film and a change in load until the ice is released by means of a load cell. The maximum load is defined as the snow sticking shearing force of the film sample tested. Shearing stresses were measured of a sample obtained by spraying a coating composition containing 0.5% by volume of perfluorinated polyether (molecular weight: 2,700) as an additive and the sample of Comparative Embodiment 1. The measurement was repeated 5 times each and average values were calculated. The coating film of Embodiment 1 had a snow sticking shearing stress of 23 g/cm² while the sample of Comparative Embodiment 1 had a snow sticking shearing stress of 55 g/cm². Thus, it was confirmed that the coating composition of the present invention had a snow sticking shearing stress smaller than the two-component coating composition of Comparative Embodiment 1 and snow deposited on the coating film made from the coating composition of the present invention released readily. Therefore, the present invention is superior in improvement of water repellent properties of coating composition and film over the prior art.

25 Next, in Embodiments 2 to 31 and Comparative Embodiments 2 to 31 below, were examined deterioration with time of water repellent properties of coating films containing various kinds of fluorocarbon polymer powders, binders and additives.

EMBODIMENT 2

30 Polytetrafluoroethylene (molecular weight: 8,500, average particle diameter: 1 μm) as a fluorocarbon polymer powder, polyvinylidene fluoride as a binder, and perfluorinated polyether (molecular weight: 2,700) as an additive were mixed in the proportions shown in Table 2-1 in a ball mill to prepare fluorocarbon polymer coating compositions containing various amounts of the additive. These fluorocarbon polymer coating compositions were sprayed on respective FRP plates comprised mainly by an epoxy resin to prepare coating film samples for evaluation of the effect of the present invention. Table 2-1 shows the compositions of samples A to C of Embodiment 2 in which the content (volume percentage) of the polyvinylidene fluoride and perfluorinated polyether were varied.

COMPARATIVE EMBODIMENT 2

35 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polyvinylidene fluoride as a binder were mixed to prepare a fluorocarbon polymer coating composition. The fluorocarbon polymer coating composition thus obtained was sprayed on an FRP plate comprised mainly by an epoxy resin to prepare a coating film sample for evaluation of its water repellent properties.

Table 2-1 shows the composition of the comparative coating film sample V1.

EMBODIMENT 3

5 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that polytetrafluoroethylene was used as the binder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-1 shows the compositions of sample films D, E, and F with varied amounts of polytetrafluoroethylene as the binder and perfluorinated polyether as the additive.

10 COMPARATIVE EMBODIMENT 3

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polytetrafluoroethylene as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-1 shows the composition of the comparative coating film sample V2.

15 EMBODIMENT 4

20 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that acrylic silicone resin was used as the binder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-1 shows the compositions of sample films G, H and I with varied amounts of acrylic silicone resin as the binder and perfluorinated polyether as the additive.

25 COMPARATIVE EMBODIMENT 4

25 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of acrylic silicone resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-1 shows the composition of the comparative coating film sample V3.

30 EMBODIMENT 5

35 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that polyester resin was used as the binder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-1 shows the compositions of sample films J, K and L with varied amounts of polyester resin as the binder and perfluorinated polyether as the additive.

COMPARATIVE EMBODIMENT 5

40 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polyester resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-1 shows the composition of the comparative coating film sample V4.

45 EMBODIMENT 6

50 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that epoxy resin was used as the binder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-1 shows the compositions of sample films M, N and O with varied amounts of epoxy resin as the binder and perfluorinated polyether as the additive.

COMPARATIVE EMBODIMENT 6

55 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of epoxy resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-1 shows the composition of the comparative coating film sample V5.

EMBODIMENT 7

5 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that perfluorinated alkyl polyether was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-2 shows the compositions of sample films A-1, B-1 and C-1 with varied amounts of polyvinylidene fluoride as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 7

10 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polyvinylidene fluoride as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-2 shows the composition of the comparative coating film sample V6.

15 EMBODIMENT 8

20 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 3 except that perfluorinated alkyl polyether as used in Embodiment 7 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-2 shows the compositions of sample films D-1, E-1 and F-1 with varied amounts of polytetrafluoroethylene as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 8

25 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polytetrafluoroethylene as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-2 shows the composition of the comparative coating film sample V7.

30 EMBODIMENT 9

35 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 4 except that perfluorinated alkyl polyether as used in Embodiment 7 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-2 shows the compositions of sample films G-1, H-1 and I-1 with varied amounts of acrylic silicone resin as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 9

40 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of acrylic silicone resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-2 shows the composition of the comparative coating film sample V8.

45 EMBODIMENT 10

50 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 5 except that perfluorinated alkyl polyether as used in Embodiment 7 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-2 shows the compositions of sample films J-1, K-1 and L-1 with varied amounts of polyester resin as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 10

55 Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polyester resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-2 shows the composition of the comparative coating film sample V9.

EMBODIMENT 11

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 6 except that perfluorinated alkyl polyether as used in Embodiment 7 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-2 shows the compositions of sample films M-1, N-1 and O-1 with varied amounts of epoxy resin as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 11

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of epoxy resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-2 shows the composition of the comparative coating film sample V10.

EMBODIMENT 12

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that polytrifluoroethylene was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-3 shows the compositions of sample films A-2, B-2 and C-2 with varied amounts of polyvinylidene fluoride as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 12

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polyvinylidene fluoride as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-3 shows the composition of the comparative coating film sample V11.

EMBODIMENT 13

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 3 except that polytrifluoroethylene as used in Embodiment 12 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-3 shows the compositions of sample films D-2, E-2 and F-2 with varied amounts of polytetrafluoroethylene as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 13

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polytetrafluoroethylene as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-3 shows the composition of the comparative coating film sample V12.

EMBODIMENT 14

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 4 except that polytrifluoroethylene as used in Embodiment 12 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-3 shows the compositions of sample films G-2, H-2 and I-2 with varied amounts of acrylic silicone resin as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 14

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of acrylic silicone resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-3 shows the composition of the comparative coating film sample V13.

EMBODIMENT 15

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 5 except that polytrifluoroethylene as used in Embodiment 12 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-3 shows the compositions of sample films J-2, K-2 and L-2 with varied amounts of polyester resin as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 15

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of polyester resin as used in Embodiment 5 as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-3 shows the composition of the comparative coating film sample V14.

EMBODIMENT 16

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 6 except that polytrifluoroethylene as used in Embodiment 12 was used as the additive. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-3 shows the compositions of sample films M-2, N-2 and O-2 with varied amounts of epoxy resin as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 16

Eighty (80) percents by volume of the same polytetrafluoroethylene powder as used in Embodiment 2 as a fluorocarbon polymer powder and 20% by volume of epoxy resin as used in Embodiment 6 as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-3 shows the composition of the comparative coating film sample V15.

EMBODIMENT 17

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that tetrafluoroethylene/hexafluoropropylene copolymer powder was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-4 shows the compositions of sample films A-3, B-3 and C-3 with varied amounts of polyvinylidene fluoride as the binder and perfluorinated polyether as the additive.

COMPARATIVE EMBODIMENT 17

Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoroethylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polyvinylidene fluoride as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-4 shows the composition of the comparative coating film sample V16.

EMBODIMENT 18

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 3 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-4 shows the compositions of sample films D-3, E-3, and F-3 with varied amounts of polytetrafluoroethylene as the binder and perfluorinated polyether as the additive.

COMPARATIVE EMBODIMENT 18

Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polytetrafluoroethylene as a binder were

mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-4 shows the composition of the comparative coating film sample V17.

5 EMBODIMENT 19

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 4 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 10 2. Table 2-4 shows the compositions of sample films G-3, H-3 and I-3 with varied amounts of acrylic silicone resin as the binder and perfluorinated polyether as the additive.

COMPARATIVE EMBODIMENT 19

15 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of acrylic silicone resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-4 shows the composition of the comparative coating film sample V18.

20 EMBODIMENT 20

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 5 except that 25 tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-4 shows the compositions of sample films J-3, K-3 and L-3 with varied amounts of polyester resin as the binder and perfluorinated polyether as the additive.

COMPARATIVE EMBODIMENT 20

30 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polyester resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-4 shows the composition of the comparative 35 coating film sample V19.

EMBODIMENT 21

40 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 6 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-4 shows the compositions of sample films M, N and O with varied amounts of epoxy resin as the binder and perfluorinated polyether as the additive.

45 COMPARATIVE EMBODIMENT 21

50 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder and 20% by volume of epoxy resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-4 shows the composition of the comparative coating film sample V20.

EMBODIMENT 22

55 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 7 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-5 shows the compositions of sample films A-4, B-4 and C-4 with varied amounts of polyvinylidene fluoride

as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 22

5 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene powder as used in Embodiment 17 was used as a fluorocarbon polymer powder and 20% by volume of polyvinylidene fluoride as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-5 shows the composition of the comparative coating film sample V21.

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EMBODIMENT 23

15 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 8 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-5 shows the compositions of sample films D-4, E-4 and F-4 with varied amounts of polytetrafluoroethylene as the binder and perfluorinated alkyl polyether as the additive.

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COMPARATIVE EMBODIMENT 23

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Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polytetrafluoroethylene as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-5 shows the composition of the comparative coating film sample V22.

EMBODIMENT 24

30 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 9 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-5 shows the compositions of sample films G-4, H-4 and I-4 with varied amounts of acrylic silicone resin as the binder and perfluorinated alkyl polyether as the additive.

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COMPARATIVE EMBODIMENT 24

40 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of acrylic silicone resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-5 shows the composition of the comparative coating film sample V23.

EMBODIMENT 25

45 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 10 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-5 shows the compositions of sample films J-4, K-4 and L-4 with varied amounts of polyester resin as the binder and perfluorinated alkyl polyether as the additive.

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COMPARATIVE EMBODIMENT 25

55 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polyester resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-5 shows the composition of the comparative coating film sample V24.

EMBODIMENT 26

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 11 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-5 shows the compositions of sample films M-4, N-4 and O-4 with varied amounts of epoxy resin as the binder and perfluorinated alkyl polyether as the additive.

COMPARATIVE EMBODIMENT 26

Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of epoxy resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-5 shows the composition of the comparative coating film sample V25.

EMBODIMENT 27

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 2 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-6 shows the compositions of sample films A-5, B-5 and C-5 with varied amounts of polyvinylidene fluoride as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 27

Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polyvinylidene fluoride as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-6 shows the composition of the comparative coating film sample V26.

EMBODIMENT 28

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 13 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-6 shows the compositions of sample films D-5, E-5 and F-5 with varied amounts of polytetrafluoroethylene as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 28

Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polytetrafluoroethylene as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-6 shows the composition of the comparative coating film sample V27.

EMBODIMENT 29

Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 14 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-6 shows the compositions of sample films G-5, H-5 and I-5 with varied amounts of acrylic silicone resin as the binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 29

5 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of acrylic silicone resin as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-6 shows the composition of the comparative coating film sample V28.

EMBODIMENT 30

10 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 15 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-6 shows the compositions of sample films J-5, K-5 and L-5 with varied amounts of polyester resin as the 15 binder and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 30

20 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of polyester resin as used in Embodiment 5 as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-6 shows the composition of the comparative coating film sample V29.

EMBODIMENT 31

25 Fluorocarbon polymer coating compositions were prepared in the same manner as in Embodiment 16 except that tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 was used as the fluorocarbon polymer powder. Coating films were prepared from these coating compositions in the same manner as in Embodiment 2. Table 2-6 shows the compositions of sample films M-5, N-5 and O-5 with varied amounts of epoxy resin as the binder 30 and polytrifluoroethylene as the additive.

COMPARATIVE EMBODIMENT 31

35 Eighty (80) percents by volume of the same tetrafluoroethylene/hexafluoropropylene copolymer powder as used in Embodiment 17 as a fluorocarbon polymer powder and 20% by volume of epoxy resin as used in Embodiment 6 as a binder were mixed to prepare a fluorocarbon polymer coating composition. A coating film from this fluorocarbon polymer coating composition was prepared in the same manner as in Embodiment 2. Table 2-6 shows the composition of the comparative coating film sample V30.

40 In Tables 2-1 to 2-6 below, the following abbreviations were used.

Abbreviation	Name of Compound
4FE	Polytetrafluoroethylene
4FE/6FP	Tetrafluoroethylene/hexafluoropropylene copolymer
FV	Polyvinylidene fluoride
AS	Acrylic silicone resin
PE	Polyester resin
EP	Epoxy resin
PFPE	Perfluorinated polyether
PFAPE	Perfluorinated alkyl polyether
3FE	Polytrifluoroethylene

Table 2-1

	FLUOROCARBON POLYMER POWDER (VOL. %)						BINDER (VOL. %)			ADDITIVE (VOL. %)	
	SAMPLE	4FE	4FE/6FP	FV	4FE	AS	PE	EP	PFPE		
EXAMPLE 2	A	80	-	-	19.5	-	-	-	-	0.5	
	B	80	-	-	18.5	-	-	-	-	2.0	
	C	80	-	-	15.0	-	-	-	-	5.0	
COM. EX. 2	V1	80	-	-	20	-	-	-	-	-	
EXAMPLE 3	D	80	-	-	-	19.5	-	-	-	0.5	
	E	80	-	-	-	18.5	-	-	-	2.0	
	F	80	-	-	-	15.0	-	-	-	5.0	
COM. EX. 3	V2	80	-	-	-	20	-	-	-	-	
EXAMPLE 4	G	80	-	-	-	-	19.5	-	-	0.5	
	H	80	-	-	-	-	18.5	-	-	2.0	
	I	80	-	-	-	-	15.0	-	-	5.0	
COM. EX. 4	V3	80	-	-	-	-	20	-	-	-	
EXAMPLE 5	J	80	-	-	-	-	-	19.5	-	0.5	
	K	80	-	-	-	-	-	18.5	-	2.0	
	L	80	-	-	-	-	-	15.0	-	5.0	
COM. EX. 5	V4	80	-	-	-	-	-	20	-	-	
EXAMPLE 6	M	80	-	-	-	-	-	-	19.5	0.5	
	N	80	-	-	-	-	-	-	18.5	2.0	
	O	80	-	-	-	-	-	-	15.0	5.0	
COM. EX. 6	V5	80	-	-	-	-	-	-	20	-	

Table 2-2

	FLUOROCARBON POLYMER POWDER (VOL. %)			BINDER (VOL. %)			ADDITIVE (VOL. %)		
	SAMPLE	4FE	4FE/6FP	FV	4FE	AS	PE	EP	PFAPE
EXAMPLE 7	A-1	80	-	19.5	-	-	-	-	0.5
	B-1	80	-	18.5	-	-	-	-	2.0
	C-1	80	-	15.0	-	-	-	-	5.0
COM. EX. 7	V6	80	-	20	-	-	-	-	-
EXAMPLE 8	D-1	80	-	-	19.5	-	-	-	0.5
	E-1	80	-	-	18.5	-	-	-	2.0
	F-1	80	-	-	15.0	-	-	-	5.0
COM. EX. 8	V7	80	-	-	20	-	-	-	-
EXAMPLE 9	G-1	80	-	-	-	19.5	-	-	0.5
	H-1	80	-	-	-	18.5	-	-	2.0
	I-1	80	-	-	-	15.0	-	-	5.0
COM. EX. 9	V8	80	-	-	-	20	-	-	-
EXAMPLE 10	J-1	80	-	-	-	-	19.5	-	0.5
	K-1	80	-	-	-	-	18.5	-	2.0
	L-1	80	-	-	-	-	15.0	-	5.0
COM. EX. 10	V9	80	-	-	-	-	20	-	-
EXAMPLE 11	M-1	80	-	-	-	-	-	19.5	0.5
	N-1	80	-	-	-	-	-	18.5	2.0
	O-1	80	-	-	-	-	-	15.0	5.0
COM. EX. 11	V10	80	-	-	-	-	-	20	-

Table 2-3

	FLUOROCARBON POLYMER POWDER (VOL. %)			BINDER (VOL. %)			ADDITIVE (VOL. %)		
SAMPLE	4FE	4FE/6FP	FV	4FE	AS	PE	EP	3F3	
EXAMPLE 12	A-2	80	-	19.5	-	-	-	0.5	
	B-2	80	-	18.5	-	-	-	2.0	
	C-2	80	-	15.0	-	-	-	5.0	
COM. EX. 12	V11	80	-	20	-	-	-	-	
EXAMPLE 13	D-2	80	-	19.5	-	-	-	0.5	
	E-2	80	-	18.5	-	-	-	2.0	
	F-2	80	-	15.0	-	-	-	5.0	
COM. EX. 13	V12	80	-	20	-	-	-	-	
EXAMPLE 14	G-1	80	-	-	19.5	-	-	0.5	
	H-1	80	-	-	18.5	-	-	2.0	
	I-1	80	-	-	15.0	-	-	5.0	
COM. EX. 14	V13	80	-	-	20	-	-	-	
EXAMPLE 15	J-2	80	-	-	-	19.5	-	0.5	
	K-2	80	-	-	-	18.5	-	2.0	
	L-2	80	-	-	-	15.0	-	5.0	
COM. EX. 15	V14	80	-	-	-	20	-	-	
EXAMPLE 16	M-2	80	-	-	-	-	19.5	0.5	
	N-2	80	-	-	-	-	18.5	2.0	
	O-2	80	-	-	-	-	15.0	5.0	
COM. EX. 16	V15	80	-	-	-	-	20	-	

Table 2-4

	FLUOROCARBON POLYMER POWDER (VOL. %)			BINDER (VOL. %)			ADDITIVE (VOL. %)		
SAMPLE	4FE	4FE/6FP	FV	4FE	AS	PE	EP	PFPE	
EXAMPLE 17	A-3	-	80	19.5	-	-	-	-	0.5
	B-3	-	80	18.5	-	-	-	-	2.0
	C-3	-	80	15.0	-	-	-	-	5.0
COM. EX. 17	V16	-	80	20	-	-	-	-	-
EXAMPLE 18	D-3	-	80	-	19.5	-	-	-	0.5
	E-3	-	80	-	18.5	-	-	-	2.0
	F-3	-	80	-	15.0	-	-	-	5.0
COM. EX. 18	V17	-	80	-	20	-	-	-	-
EXAMPLE 19	G-3	-	80	-	-	19.5	-	-	0.5
	H-3	-	80	-	-	18.5	-	-	2.0
	I-3	-	80	-	-	15.0	-	-	5.0
COM. EX. 19	V18	-	80	-	-	20	-	-	-
EXAMPLE 20	J-3	-	80	-	-	-	19.5	-	0.5
	K-3	-	80	-	-	-	18.5	-	2.0
	L-3	-	80	-	-	-	15.0	-	5.0
COM. EX. 20	V19	-	80	-	-	-	20	-	-
EXAMPLE 21	M-3	-	80	-	-	-	-	19.5	0.5
	N-3	-	80	-	-	-	-	18.5	2.0
	O-3	-	80	-	-	-	-	15.0	5.0
COM. EX. 21	V20	-	80	-	-	-	-	20	-

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Table 2-5

	FLUOROCARBON POLYMER POWDER (VOL. %)			BINDER (VOL. %)			ADDITIVE (VOL. %)		
SAMPLE	4FE	4FE/6FP	FV	4FE	AS	PE	EP	PFAPE	
EXAMPLE 22	A-4	-	80	19.5	-	-	-	-	0.5
	B-4	-	80	18.5	-	-	-	-	2.0
	C-4	-	80	15.0	-	-	-	-	5.0
COM. EX. 22	V21	-	80	20	-	-	-	-	-
EXAMPLE 23	D-4	-	80	-	19.5	-	-	-	0.5
	E-4	-	80	-	18.5	-	-	-	2.0
	F-4	-	80	-	15.0	-	-	-	5.0
COM. EX. 23	V22	-	80	-	20	-	-	-	-
EXAMPLE 24	G-4	-	80	-	-	19.5	-	-	0.5
	H-4	-	80	-	-	18.5	-	-	2.0
	I-4	-	80	-	-	15.0	-	-	5.0
COM. EX. 24	V23	-	80	-	-	20	-	-	-
EXAMPLE 25	J-4	-	80	-	-	-	19.5	-	0.5
	K-4	-	80	-	-	-	18.5	-	2.0
	L-4	-	80	-	-	-	15.0	-	5.0
COM. EX. 25	V24	-	80	-	-	-	20	-	-
EXAMPLE 26	M-4	-	80	-	-	-	-	19.5	0.5
	N-4	-	80	-	-	-	-	18.5	2.0
	O-4	-	80	-	-	-	-	15.0	5.0
COM. EX. 26	V25	-	80	-	-	-	-	20	-

Table 2-6

	FLUOROCARBON POLYMER POWDER (VOL. %)				BINDER (VOL. %)			ADDITIVE (VOL. %)	
	SAMPLE	4FE	4FE/6FP	FV	4FE	AS	PE	EP	3FE
EXAMPLE 27	A-5	-	80	19.5	-	-	-	-	0.5
	B-5	-	80	18.5	-	-	-	-	2.0
	C-5	-	80	15.0	-	-	-	-	5.0
COM. EX. 27	V26	-	80	20	-	-	-	-	-
EXAMPLE 28	D-5	-	80	-	19.5	-	-	-	0.5
	E-5	-	80	-	18.5	-	-	-	2.0
	F-5	-	80	-	15.0	-	-	-	5.0
COM. EX. 28	V27	-	80	-	20	-	-	-	-
EXAMPLE 29	G-5	-	80	-	-	19.5	-	-	0.5
	H-5	-	80	-	-	18.5	-	-	2.0
	I-5	-	80	-	-	15.0	-	-	5.0
COM. EX. 29	V28	-	80	-	-	20	-	-	-
EXAMPLE 30	J-5	-	80	-	-	-	19.5	-	0.5
	K-5	-	80	-	-	-	18.5	-	2.0
	L-5	-	80	-	-	-	15.0	-	5.0
COM. EX. 30	V29	-	80	-	-	-	20	-	-
EXAMPLE 31	M-5	-	80	-	-	-	-	19.5	0.5
	N-5	-	80	-	-	-	-	18.5	2.0
	O-5	-	80	-	-	-	-	15.0	5.0
COM. EX. 31	V30	-	80	-	-	-	-	20	-

TEST EXAMPLE 4

In the same manner as in TEST EXAMPLE 1 were measured the water repellent properties of the coating film samples of Embodiments 2 to 6 and Comparative Embodiments 2 to 6. As a result, all the coating film samples A to O of Embodiments 2 to 6 and coating film samples V1 to V5 of Comparative Embodiments 2 to 6 showed a water contact angle of about 150°. Therefore, no substantial difference was observed in initial water repellent properties between the samples of Embodiments 2 to 6 and the comparative samples of Comparative Embodiments 2 to 6.

Next, deterioration with time of water repellent properties of coating films will be described hereinbelow. The coating films samples A to O of Embodiments 2 to 6 and comparative film samples V1 to V5 of Comparative Embodiments 2 to 6 were immersed in deionized water and taken out of the water after predetermined period (days), followed by measuring water contact angles in the same manner as described in above. This operation was repeated and influences of long-term water immersion were evaluated. Figs. 5A, 5B, 5C, 5D and 5E show the results obtained. In Figs. 5A, 5B, 5C, 5D and 5E, blank circle, blank square, blank triangle indicate samples containing the additive in amounts of 0.5% by volume, 2.0% by volume, and 5.0% by volume, respectively. Filled triangle indicates the sample which contain 0% by volume of the additive. The fluorocarbon polymer coating films of Embodiments 2 to 6 show a less decrease in water repellent properties with time than the coating films of Comparative Embodiments 2 to 6. Upon measurement of water contact angle, the coating films of Embodiments 2 to 6 showed a water contact angle of 150° just after formation of the films. Therefore, comparing initial water repellent properties, there was observed no substantial difference between the samples of the present invention and those of comparative embodiments. However, as for long-term resistance to water immersion, the fluorocarbon polymer coating composition is superior to the conventional fluorocarbon polymer coating composition.

Further, similar water repellency tests were conducted on samples A-1 to O-1, A-2 to O-2, A-3 to O-3, A-4 to O-4, and A-5 to O-5 of Embodiments 7 to 31 as well as samples V6 to V30 of Comparative Embodiments 7 to 31 in the same manner as in TEST EXAMPLE 1. Results similar to those obtained with the samples of Embodiments 2 to 6 and Comparative Embodiments 2 to 6 were obtained.

Fig. 6 illustrates influence of the amount of the perfluorinated polyether on residual water repellent properties after 200 day water immersion, as an index of long-term durability to water. In Fig. 6, symbols A_0 , B_0 and C_0 indicate the film sample groups containing 0.5% by volume, 2.0% by volume and 5.0%, respectively, by volume of perfluorinated polyether as the additive. V_0 indicates the film sample group containing no additive.

$$\text{Residual Water Repellency} = \frac{\text{Water Contact Angle After 200 Day Water Immersion}}{\text{Initial Water Contact Angle}}$$

and calculated from Figs. 5A, 5B, 5C, 5D and 5E. Fig. 6 shows that when 0.5% by volume of perfluorinated polyether is present in the coating film (cf. sample group A_0), the residual water repellent property after 200 day water immersion is at least 90%, which means long-term durability to water.

TEST EXAMPLE 5

Next, in order to examine correlation of the structure of the coating films with time-dependent change of water repellency, the surfaces of the coating films of samples A to C of Embodiment 2 and sample V1 of Comparative Embodiment 2 were observed. Figs. 7A, 7B, 7C and 7D are schematic diagrams illustrating the conditions of the surfaces of the coating films observed on SEM (scanning electron microscope) at a magnification of X3,000. In Figs. 7A, 7B, 7C and 7D, 3 is a fluorocarbon polymer particle, 4 is a binder, and 5 is an agglomerate. As shown in Figs. 7B, 7C and 7D schematically illustrating the surface of the film samples A to C, addition of perfluorinated polyether cause the fluorocarbon polymer particles 3 to be taken up by the binder (or fluoro oil as the additive) 4 and agglomerate to form a fluorocarbon polymer coating composition containing fluorocarbon polymer powder consisting of particles with gaps therebetween being filled with the binder or fluoro oil. This phenomenon is remarkable in samples B and C. The surface of the agglomerate 5 is covered with the fluorocarbon polymer particles 3. The above-described results suggest that this particular structure of the coating film as observed in the samples of Embodiment 2 contribute to long-term durability to water.

To further examine whether the configuration of the surface of the coating film as illustrated in Figs. 7A, 7B, 7C or 7D is also retained inside the coating film, cross-section of the coating film was observed on SEM. Figs. 8A, 8B, 8C and 8D are schematic diagrams illustrating the profile of the film samples A to C of Embodiment 2 and sample V1 of Comparative Embodiment 2 observed on SEM at a magnification of X1,000. The FRP plate was notched and applied shearing force to cut. The resulting cross section was used as a sample for observing the profile of the coating film. In the sample of Comparative Embodiment 2, no agglomeration of the fluorocarbon polymer powder was observed from the surface to the inside of the coating film. On the other hand, addition of perfluorinated polyether resulted in the

agglomeration of the fluorocarbon polymer powder. Particularly in the sample C, remarkable agglomeration can be observed which prevails from the surface to just above the FRP substrate. In the samples A and B where no remarkable agglomeration was observed, breakage occurred between the fluorocarbon polymer particles, which indicates that the binder or fluoro oil (additive) fills the gaps between the particles.

For quantifying the conditions of agglomeration of the fluorocarbon polymer powder as observed by the above-described surface and profile observations, measurement was made of surface roughness of the film samples A to C of Embodiment 2 and sample V1 of Comparative Embodiment 2. Surface roughness was measured using a surface roughness tester manufactured by TOKYO SEIMITSU CO., LTD. by the method according to JIS B 0601 (Japan Standard Association; JIS HANDBOOK 34, Metal Surface Treatment, Item 17 (1994). Figs. 9A, 9B, 9C and 9D show surface roughness curves and scales in 2-dimensional measurement for the respective samples. Table 3 shows ten-point average surface roughness values (JIS B 0601).

Table 3

Sample	Ten Point Average Surface Roughness (μm)
Example A	7.1
B	17.4
C	19.5
Comparative Example	2.8

From the results shown above, increasing amounts of perfluorinated polyether results in increased surface roughness values. This increase in surface roughness, as illustrated in Figs. 7B, 7C and 7D and Figs. 8B, 8C and 8D, is considered to correspond to the phenomenon that the fluorocarbon polymer powder is being incorporated in the additive or binder to agglomerate.

From the above-described results, the coating films of the present invention that contains an additive in addition to the fluorocarbon polymer powder and the binder has a specific structure that the fluorocarbon polymer particles agglomerate to form agglomerated units to fill the gaps between the fluorocarbon polymer particles so that a decrease in water repellency after prolonged immersion in water can be prevented effectively.

EMBODIMENT 32

Polytetrafluoroethylene powder (M.W.: 8,500, average particle diameter: 1 μm) was prepared under atmosphere of not higher than 0.1% oxygen with an increased degree of fluorination. The thus prepared fluorocarbon polymer powder (H) floated on the surface of 5% acetone water. The fluorocarbon polymer powder (H), polyvinylidene fluoride as a binder and perfluorinated polyether (M.W.: 2,700) as an additive were mixed in a ball mill to prepare coating compositions. These coating compositions were sprayed onto respective FRP plates comprised mainly by an epoxy resin to form coating films for evaluation of the effect of the present invention. Table 4 shows the compositions of samples A-6 to C-6 in which the content (volume percentage) of the polyvinylidene fluoride as a binder and perfluorinated polyether as an additive were varied.

Furthermore, another type of polytetrafluoroethylene powder (M.W.: 8,500, average particle diameter 1 μm) was prepared without controlling increasing the degree of fluorination and controlling the concentration of oxygen in the ambient atmosphere. The thus obtained fluorocarbon polymer powder (L) settled to the bottom in 5% acetone water. The coating compositions were prepared in the same manner as described above except that use was made of the fluorocarbon polymer powder (L). The resulting coating compositions were sprayed onto respective FRP plates comprised mainly by an epoxy resin to form coating films. Table 4 shows the compositions of samples A-7, B-7 and C-7 in which the content (volume percentage) of the polyvinylidene fluoride as a binder and perfluorinated polyether as an additive were varied.

COMPARATIVE EMBODIMENT 32

A coating film sample was prepared in the same manner as in Embodiment 32 except that no additive was used. Table 4 shows the composition of the comparative coating film sample V31 and V32.

Table 4

SAMPLE	FLUOROCARBON POLYMER POWDER (VOL. %)			BINDER (VOL. %)			ADDITIVE (VOL. %)		
	4FE (H)	4FE (L)	FV	4FE	AS	PE	EP	PFPE	
EXAMPLE 32	A-6	80	-	19.5	-	-	-	-	0.5
	B-6	80	-	18.5	-	-	-	-	2.0
	C-6	80	-	15.0	-	-	-	-	5.0
	A-7	-	80	19.5	-	-	-	-	0.5
	B-7	-	80	18.5	-	-	-	-	2.0
	C-7	-	80	15.0	-	-	-	-	5.0
COM. EX. 32	V31	80	-	20	-	-	-	-	-
	V32	-	80	20	-	-	-	-	-

TEST EXAMPLE 6

Next, deterioration with time of water repellency of samples of Embodiment 32 and Comparative Embodiment 32 were examined. The coating film samples of Embodiment 32, i.e., A-6, B-6, C-6, A-7, B-7 and C-7 and samples of Comparative Embodiment 32, i.e., V31 and V32, were immersed in deionized water and taken out therefrom after predetermined period (days) and water contact angles were measured in the same manner as described above. This operation was repeated and the results obtained were evaluated for influence of long term water immersion on the water repellent properties of the films. Figs. 10A and 10B show the results. In Figs. 10A and 10B, blank circle, blank square and blank triangle indicate the samples which contained 0.5% by volume, 2.0% by volume and 5.0% by volume, respectively, of the additive. Filled triangle indicates samples containing no additive (0% by volume). From the results, it can be seen that the fluorocarbon polymer powder (H), which was prepared with an increased degree of fluorination and under atmosphere of not higher than 0.1% of oxygen, showed substantially the same tendency of resistance to deterioration with time of water repellency as the fluorocarbon polymer powder (L), which was prepared without increasing the degree of fluorination and controlling oxygen concentration in the ambient atmosphere while the powder (H) showed an initial water contact angle of about 150° in contrast to the powder (L) which showed an initial water contact angle of about 130°. Therefore, use of the powder (H) is effective in increasing the initial water repellency of the coating films.

The present invention has been described in detail with respect to an embodiment, and it will now be apparent from the foregoing to those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects, and it is the intention, therefore, in the appended claims to cover all such changes and modifications as fall within the true spirit of the invention.

Claims

1. A fluorocarbon polymer coating composition characterized by comprising:
a fluorocarbon polymer powder;
a binder; and
an additive comprising a substance having a surface free energy smaller than that of said binder.
2. The fluorocarbon polymer coating composition as claimed in claim 1, characterized in that said additive is one substance selected from a fluoro oil, a surfactant, and mixtures thereof.
3. The fluorocarbon polymer coating composition as claimed in claim 2, characterized in that said fluoro oil is at least one of perfluorinated polyether, perfluorinated alkyl polyether, and polytrifluoroethylene.
4. The fluorocarbon polymer coating composition as claimed in claim 2, characterized in that said surfactant is a fluorocarbon surfactant.
5. The fluorocarbon polymer coating composition as claimed in claim 1, characterized in that said fluorocarbon polymer powder is at least one of polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder, and mixtures thereof.
6. The fluorocarbon polymer coating composition as claimed in claim 5, characterized in that said fluorocarbon polymer powder comprises fluorocarbon polymer having partially or completely fluorinated terminal groups.
7. The fluorocarbon polymer coating composition as claimed in claim 1, characterized in that said binder is at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, ethylene/carbon monoxide copolymer, ethylene/vinylketone copolymer, propylene/vinylketone copolymer, styrene/vinylketone and co-polymer.
8. The fluorocarbon polymer coating composition as claimed in claim 7, characterized in that said binder is at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone and polyester resin.
9. The fluorocarbon polymer coating composition as claimed in claim 1, characterized in that said additive has a surface free energy larger than that of said perfluorinated polymer powder.

10. The fluorocarbon polymer coating composition as claimed in claim 1, characterized in that said fluorocarbon polymer powder comprises fluorocarbon polymer having an average molecular weight of 500 to 20,000.

11. A fluorocarbon polymer coating film characterized by comprising:

5 a fluorocarbon polymer powder;
 a binder; and
 an additive comprising a substance having a surface free energy smaller than that of said binder.

10 12. The fluorocarbon polymer coating film as claimed in claim 11, characterized in that said additive is one substance selected from a fluoro oil, a surfactant, and mixtures thereof.

15 13. The fluorocarbon polymer coating film as claimed in claim 12, characterized in that said fluoro oil is at least one of perfluorinated polyether, perfluorinated alkyl polyether, and polytrifluoroethylene.

15 14. The fluorocarbon polymer coating film as claimed in claim 12, characterized in that said surfactant is a fluorocarbon surfactant.

20 15. The fluorocarbon polymer coating film as claimed in claim 11, characterized in that said fluorocarbon polymer powder is at least one of polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder, and mixtures thereof.

25 16. The fluorocarbon polymer coating film as claimed in claim 15, characterized in that said fluorocarbon polymer powder comprises fluorocarbon polymer having partially or completely fluorinated terminal groups.

25 17. The fluorocarbon polymer coating film as claimed in claim 11, characterized in that said binder is at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, ethylene/carbon monoxide copolymer, ethylene/vinylketone copolymer, propylene/vinylketone copolymer, styrene/vinylketone and copolymer.

30 18. The fluorocarbon polymer coating film as claimed in claim 17, characterized in that said binder is at least one of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone and polyester resin.

35 19. The fluorocarbon polymer coating film as claimed in claim 11, characterized in that said additive has a surface free energy larger than that of said perfluorinated polymer powder.

35 20. The fluorocarbon polymer coating film as claimed in claim 11, characterized in that said fluorocarbon polymer powder comprises fluorocarbon polymer having an average molecular weight of 500 to 20,000.

40 21. The fluorocarbon polymer coating film as claimed in claim 20, characterized in that said fluorocarbon polymer powder exists in agglomerate units comprised by a mixture of said fluorocarbon polymer powder with said binder or said additive, said agglomerate unit constituting said coating film.

45 22. The fluorocarbon polymer coating film as claimed in claim 20, characterized in that gaps between particles of said fluorocarbon polymer powder are filled with at least one of said binder and said additive.

45 23. A water repellent composition characterized by comprising:

50 a fluorocarbon polymer powder characterized by comprising a fluorocarbon polymer having a molecular weight of 500 to 20,000;
 a matrix resin selected from the group consisting of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, epoxy resin, ethylene/carbon monoxide, ethylene/vinylketone copolymer, propylene/vinylketone copolymer, styrene/vinylketone copolymer, and mixtures thereof; and
 an additive comprising a substance having a surface free energy smaller than that of said matrix resin.

55 24. The water repellent composition as claimed in claim 23, characterized in that said fluorocarbon polymer powder is at least one selected from the group consisting of polyvinylidene fluoride, polytetrafluoroethylene, acrylic silicone resin, polyester resin, epoxy resin, and mixtures thereof.

25. The water repellent composition as claimed in claim 23, characterized in that said additive is at least one substance selected from a fluoro oil, surfactant and mixtures thereof.

5 26. The water repellent composition as claimed in claim 25, characterized in that said fluoro oil is at least one of perfluorinated polyether, perfluorinated alkyl polyether, and polytrifluoroethylene.

27. The water repellent composition as claimed in claim 25, characterized in that said surfactant is a fluorocarbon surfactant.

10 28. The water repellent composition as claimed in claim 23, characterized in that said fluorocarbon polymer powder is at least one of polytetrafluoroethylene powder, tetrafluoroethylene/hexafluoropropylene copolymer powder, polyvinylidene fluoride powder, and mixtures thereof.

15 29. The water repellent composition as claimed in claim 28, characterized in that said fluorocarbon polymer powder comprises fluorocarbon polymer having partially or completely fluorinated terminal groups.

30. The water repellent composition as claimed in claim 23, characterized in that said additive has a surface free energy larger than that of said perfluorinated polymer powder.

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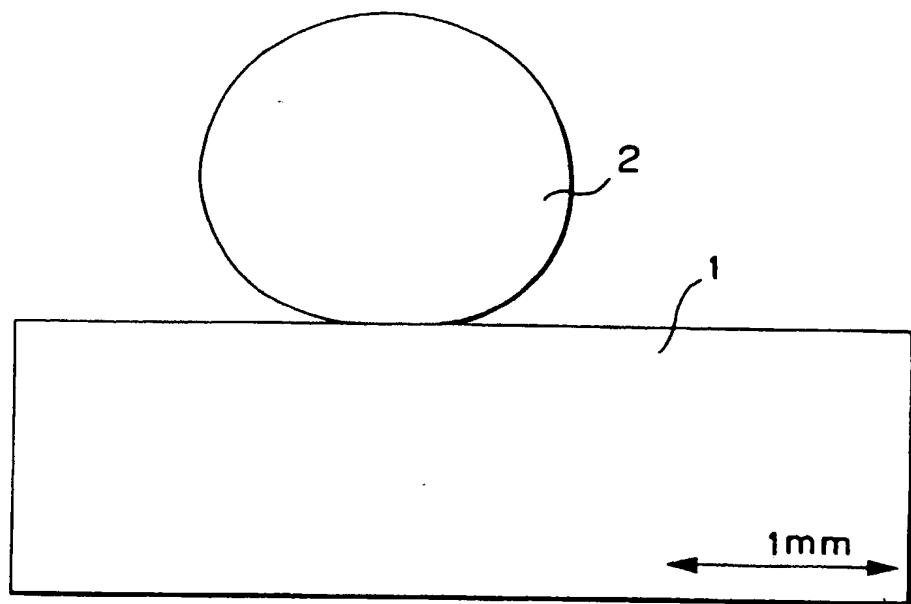


FIG. 1A

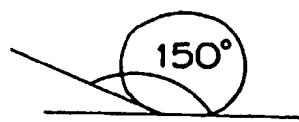


FIG. 1B

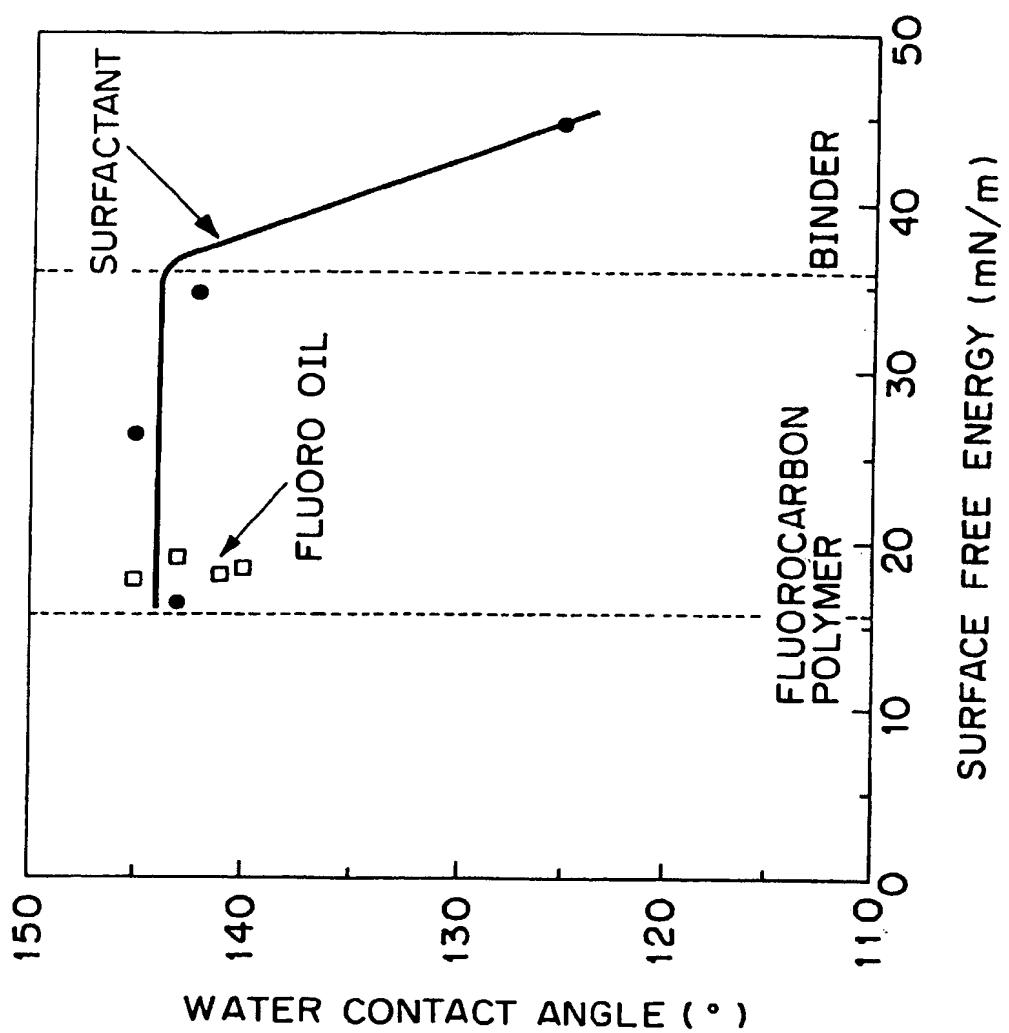


FIG.2

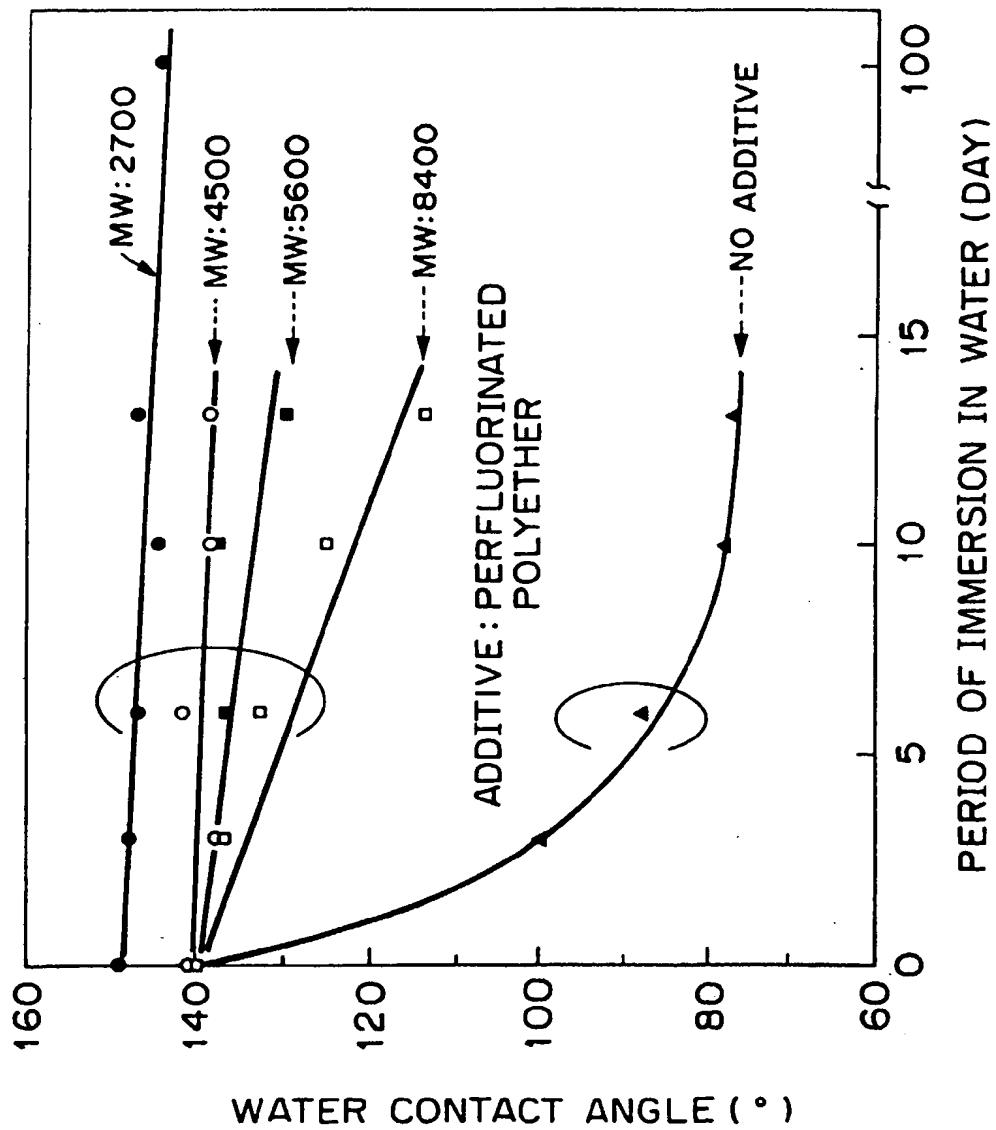


FIG. 3

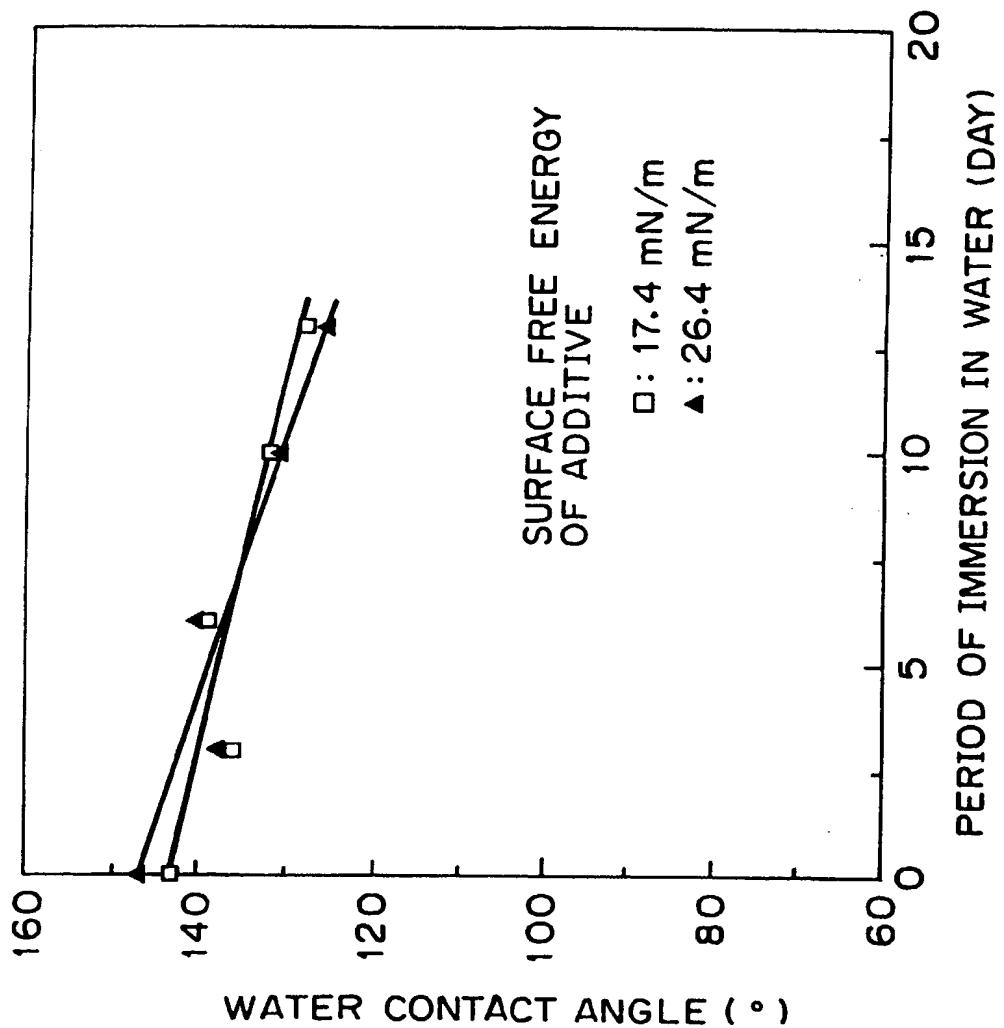


FIG. 4

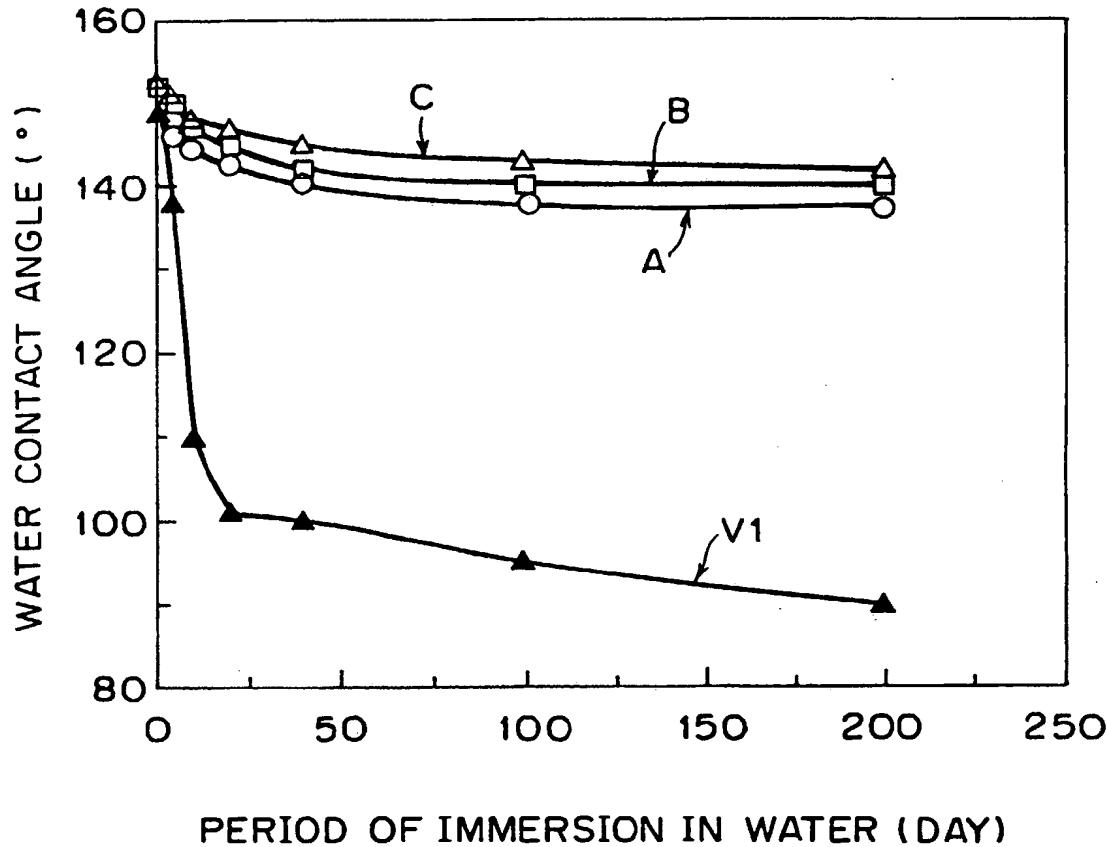


FIG.5A

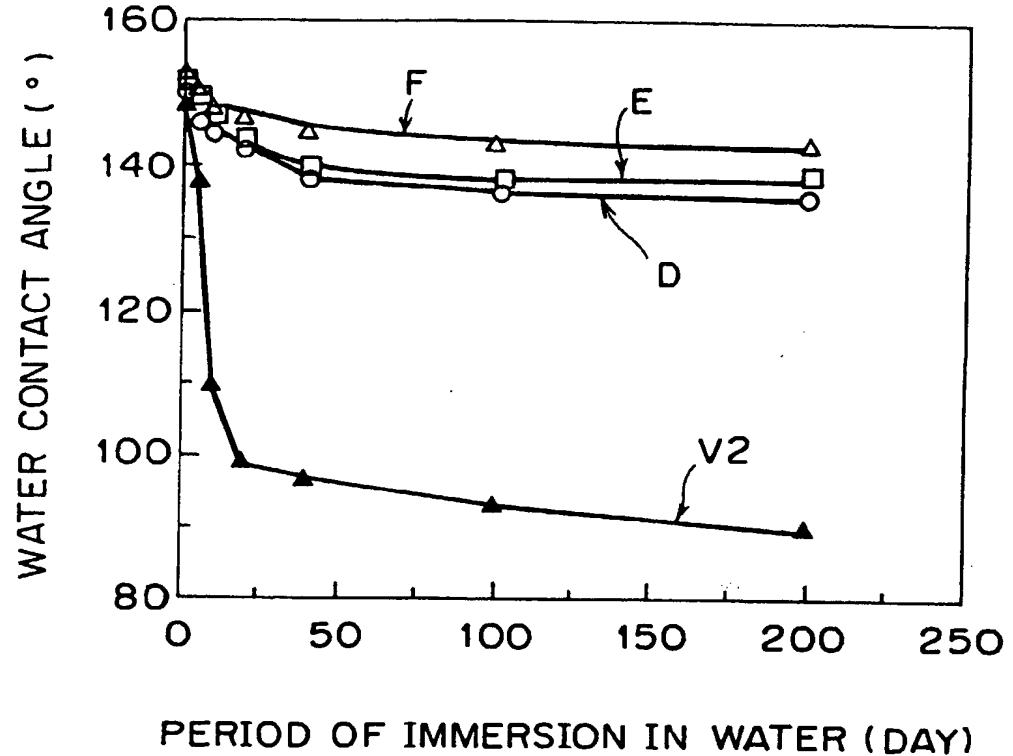


FIG.5B

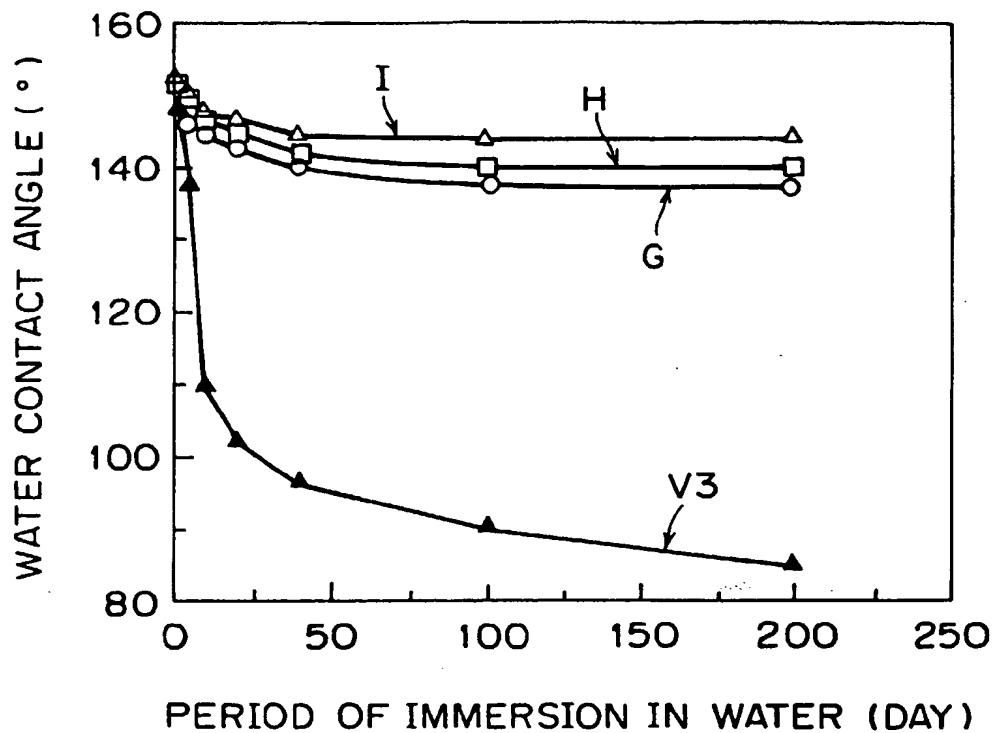


FIG.5C

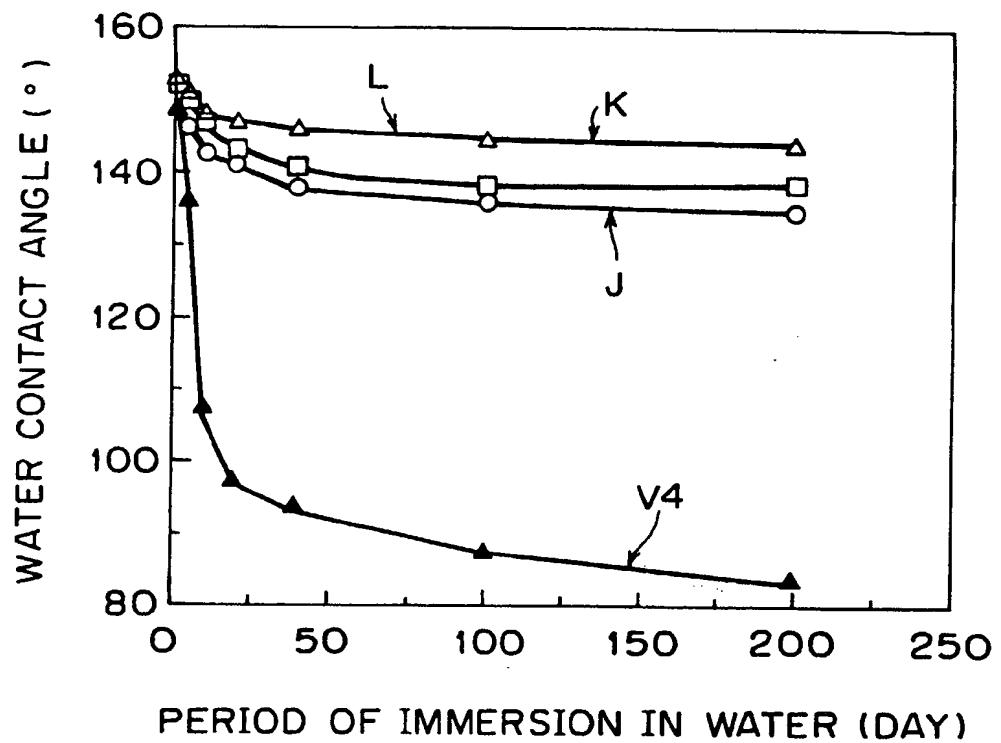


FIG.5D

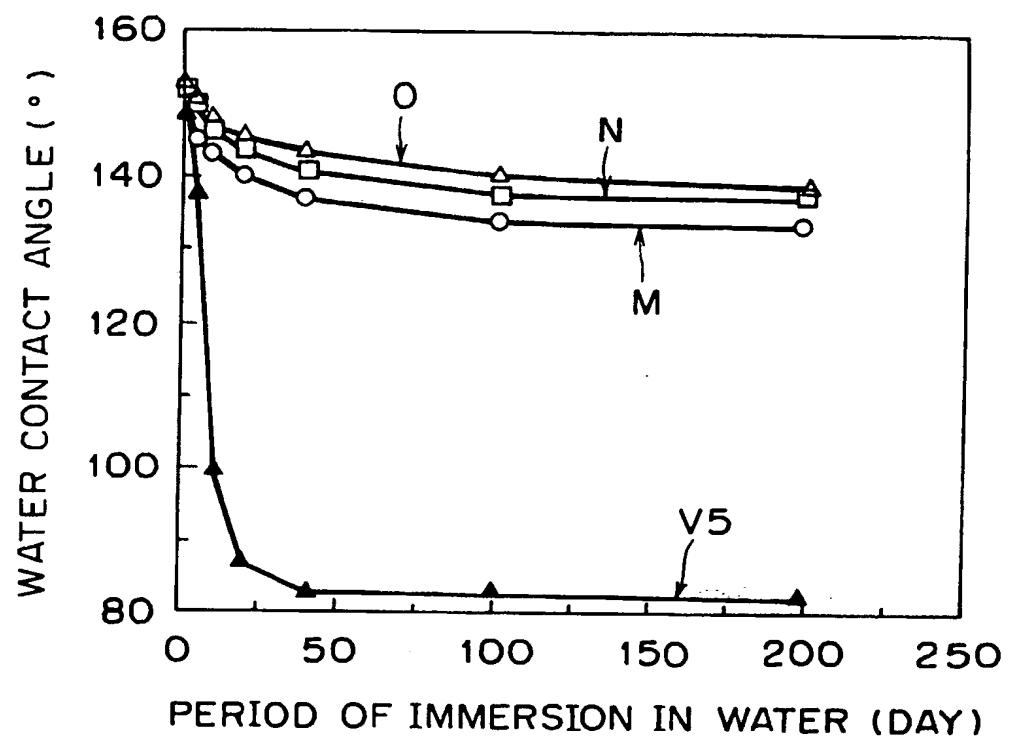


FIG.5E

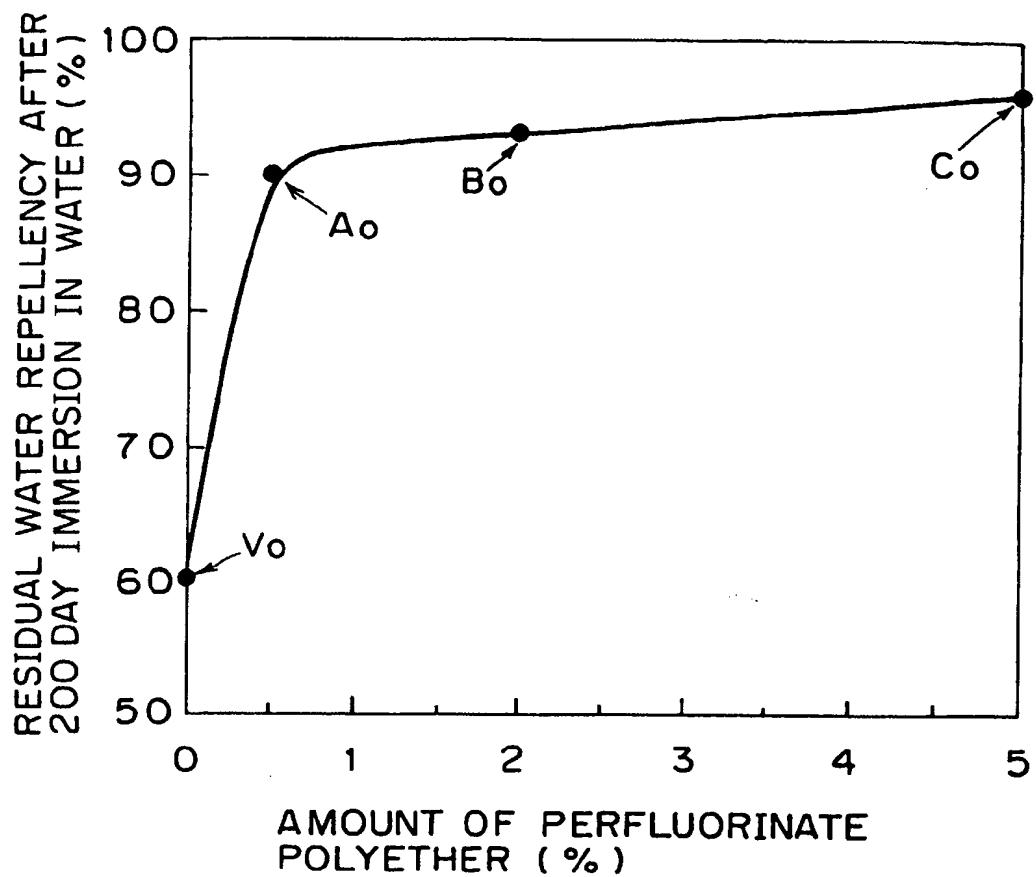


FIG.6

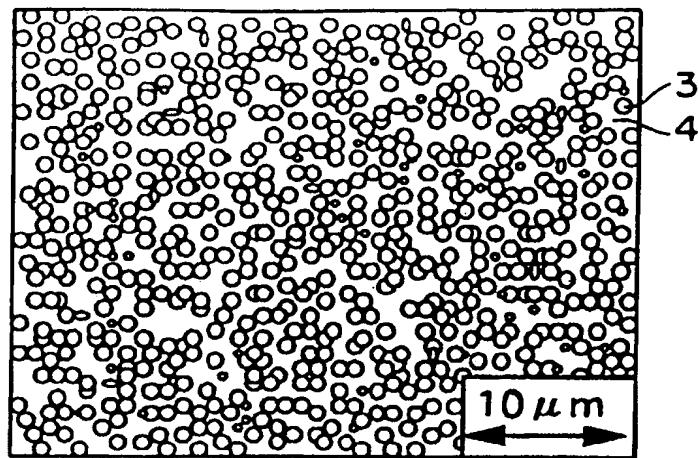


FIG. 7A

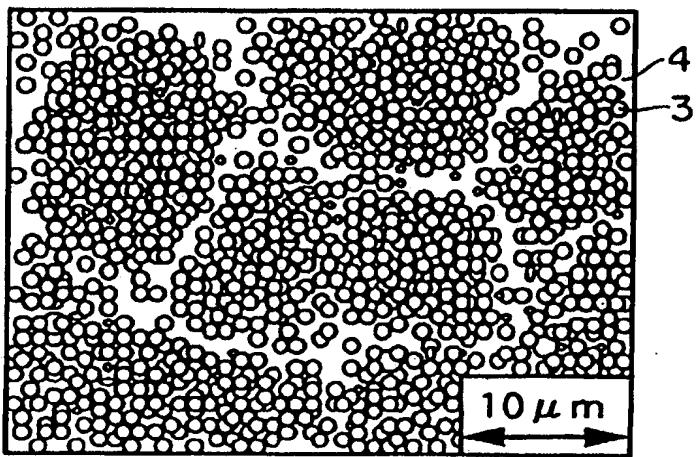


FIG. 7B

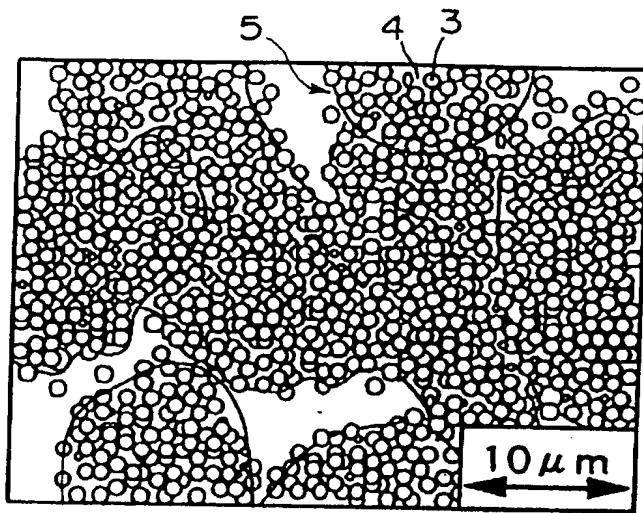


FIG.7C

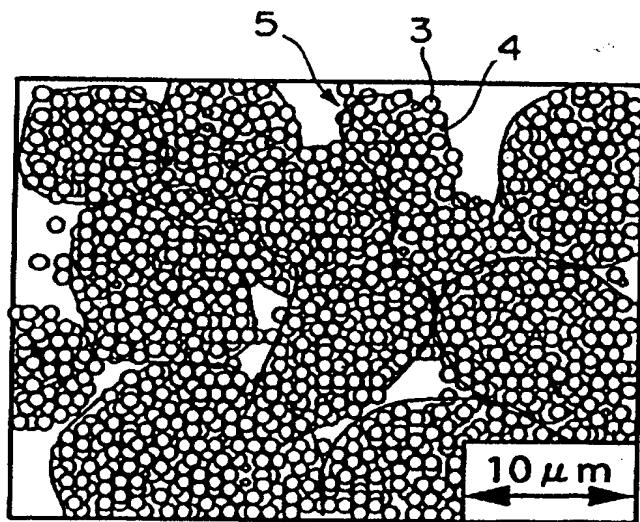


FIG.7D

FIG.8A

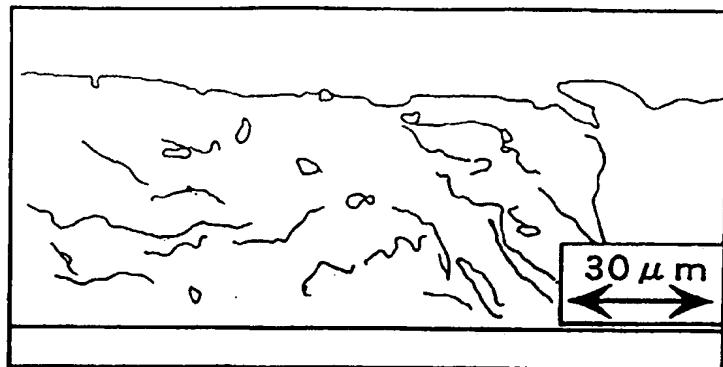


FIG.8B

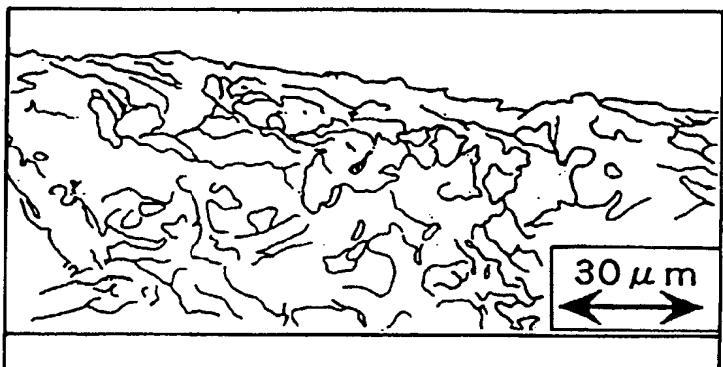


FIG.8C

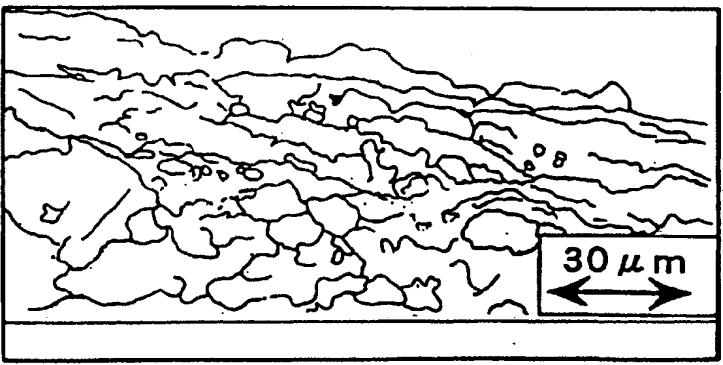
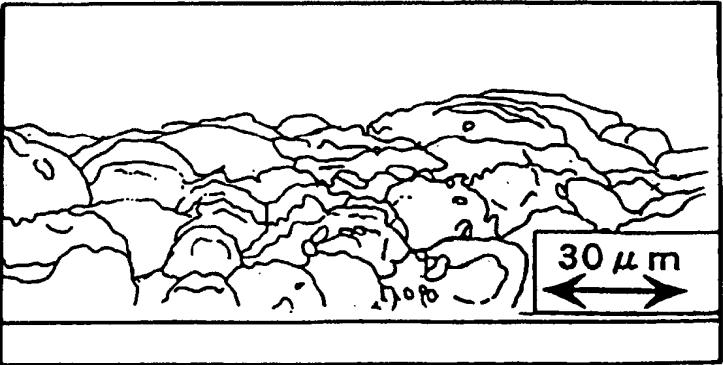


FIG.8D



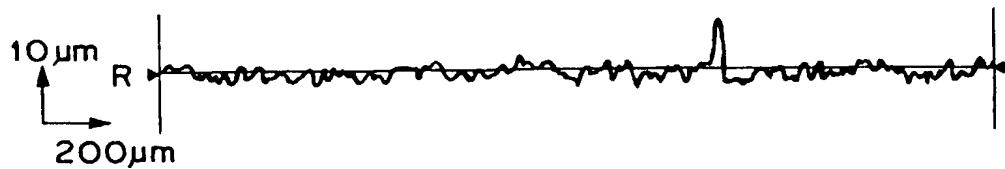


FIG.9A



FIG.9B

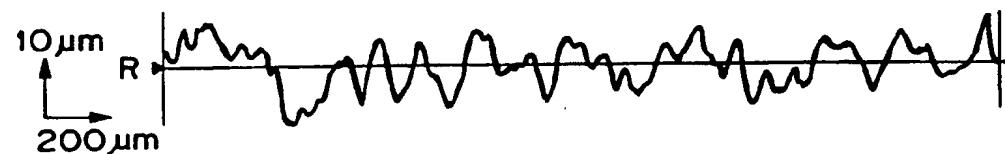


FIG.9C

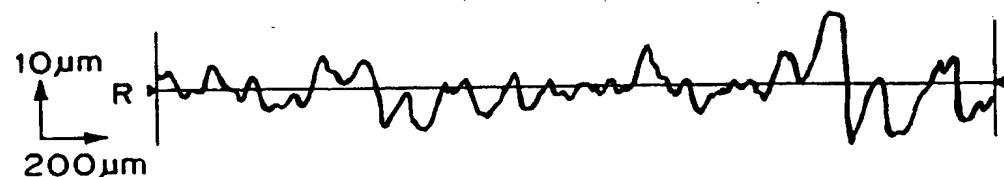


FIG.9D

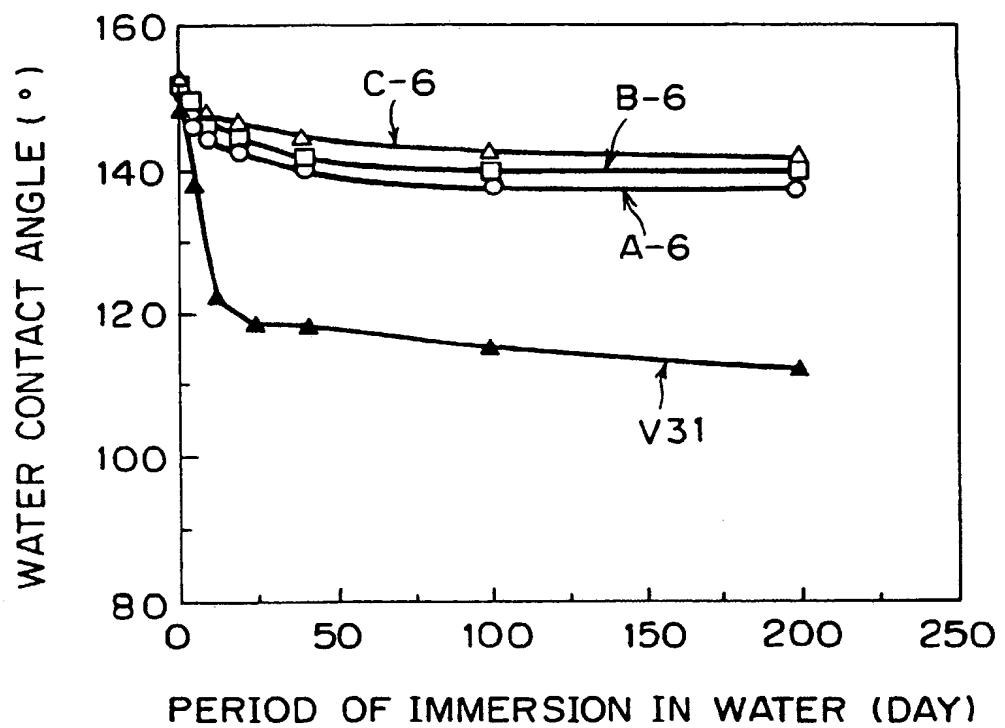


FIG.10A

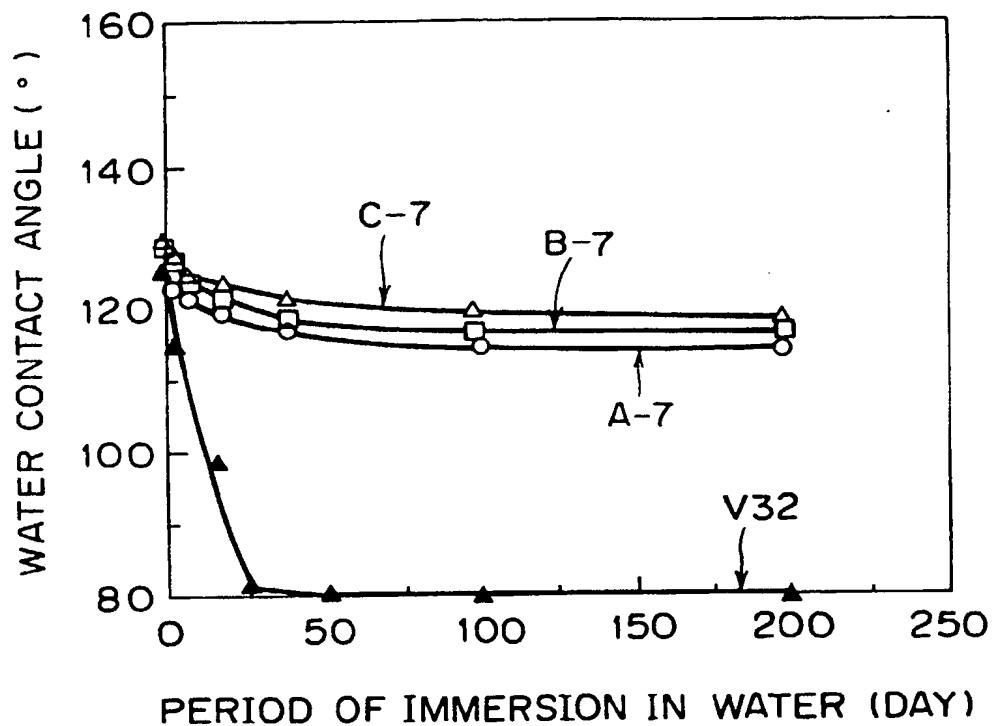


FIG. 10B



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 5262

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
X	EP-A-0 132 716 (LABORATOIRE SUISSE DE RECHERCHES HORLOGÈRES) * claims 1-3; example 9 *	1-3, 5, 6, 11-13, 15	C09D127/12 C09D127/18 C09K3/18						
A	EP-A-0 503 872 (UYEMURA & CO. ET AL) * page 2, line 47 - page 3, line 2 * * page 4, line 51 - line 56 * ---	1, 2, 5, 10, 23-25, 28							
A	DATABASE WPI Week 9440 Derwent Publications Ltd., London, GB; AN 94-322286 XP002017792 & JP-A-06 248 110 (NIPPON TELEGRAPH & TELEPHONE CORP) * abstract *	1, 5-8, 10, 23, 24, 28, 29							
A	DATABASE WPI Week 9423 Derwent Publications Ltd., London, GB; AN 94-186504 XP002017793 & JP-A-06 122 841 (NIPPON TELEGRAPH & TELEPHONE CORP) * abstract *	1, 5, 7, 8, 10, 23, 24, 28	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C09D C09K						
A P, A	WO-A-94 21729 (DAIKIN INDUSTRIES) & EP-A-0 690 096 (DAIKIN INDUSTRIES) * the whole document *	1 1							
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>6 November 1996</td> <td>Puetz, C</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	6 November 1996	Puetz, C
Place of search	Date of completion of the search	Examiner							
THE HAGUE	6 November 1996	Puetz, C							
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<small> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </small>									

